CHEM-E6180 - Fundamentals of Hydrometallurgy

**Task:** Dissolve cobalt and lithium from battery cathode material using copper as a reductant

**Group size:** 4 people

**Meeting point:** Vuorimiehentie 2, main lobby in front of reception, use the main entrance (entrance K).

**Meeting time:** 12:30

**Background**

Batteries are becoming an increasingly important means of energy storage. Various portable devices contain a battery, and in the recent years, batteries have also been used in high quantities in electric vehicles. Most of these batteries are based on lithium-ion technology. In Lithium-Ion Batteries (LIB), recharge and discharge occurs through the movement of lithium ions between the cathode and anode. The cathode consists of active cathode material attached to an aluminum current collector, whereas the anode consists of a copper current collector and carbon. The separator between the anode and cathode is made of polymers and ceramics. The electrolyte is a lithium salt (often LiPF6) in organic solvent. The active cathode material is composed of transition metals like Co, Ni and Mn.



Source: Or et al., Recycling of mixed cathode lithium‐ion batteries for electric vehicles: Current status and future outlook. Carbon Energy. 2020, 2: 6–43.

There are several types of LIBs and the main difference is in the cathode material. Lithium Cobalt Oxide (LCO) batteries have LiCoO2 cathode (~60% Co) and graphite anode. They have been available since 1991 and used in small equipment like mobile phones, laptops, cameras but not in large scale applications. Lithium Nickel Cobalt Aluminum Oxide (NCA) batteries have LiNiCoAlO2 cathode (~9% Co) and graphite anode. They have been available since 1999, and used in medical devices, industrial and electric powertrain applications. Currently they are mainly used by Panasonic and Tesla, and there is growth potential because of lower Co content. Lithium Nickel Manganese Cobalt Oxide (NMC) batteries have LiNiMnCoO2 cathode and graphite anode. They have been available since 2008, and they are used in E-bikes, medical devices, electric vehicles, and industrial applications. NMC is currently the leading system and dominant cathode chemistry. The cathode chemistries are described by NMC + three digits that give the molar ratios of Ni, Mn and Co. NMC chemistries range from NMC 111 with equal molar amounts of Ni, Mn and Co to NMC 811 with 8 parts of Ni and 1 part of both Mn and Co.

Sulfuric acid is a typical lixiviant used in hydrometallurgical recycling of waste Li-ion batteries. Dissolution of LCO in acid occurs according to the following equation:

$$4LiCoO\_{2}\left(s\right)+12H^{+}\left(aq\right) \rightarrow 4Li^{+}\left(aq\right)+4Co^{2+}\left(aq\right)+6H\_{2}O(l)+O\_{2}(g)$$

However, LCO only dissolves spontaneously in sulfuric acid up to a certain point, after which a reductant is needed for the leaching to proceed. One leaching system that has been studied in the group of Hydrometallurgy and corrosion uses copper as a reductant and iron as a catalyst to transfer electrons between LCO and Cu. The principle of this leaching system is described below.

Iron acts as a reductant towards LCO (Co3+ 🡪 Co2+) and oxidizes to Fe3+:

$$LiCoO\_{2}\left(s\right)+4H^{+}\left(aq\right)+Fe^{2+}(aq) \rightarrow Li^{+}\left(aq\right)+Co^{2+}\left(aq\right)+2H\_{2}O\left(l\right)+Fe^{3+}(aq)$$

Copper ‘regenerates’ iron by reducing it back to Fe2+ state and dissolving in the process:

$$2Fe^{3+}(aq)+Cu\left(s\right)\rightarrow 2Fe^{2+}(aq)+Cu^{2+}(aq)$$

By combining the two equations, the total reaction can be presented as follows:

$$2LiCoO\_{2}\left(s\right)+8H^{+}\left(aq\right)+Cu(s) →2Li^{+}\left(aq\right)+2Co^{2+}\left(aq\right)+4H\_{2}O\left(l\right)+Cu^{2+}(aq)$$

Copper is used as current collector in the anode side of the battery, and the casings of battery cells are made of steel. As a result, both copper and iron are present in crushed battery waste, which makes utilizing them as a reductant and catalyst attractive.

**Experimental**

The goal of this laboratory exercise is to leach Li and Co out of pure commercial LCO in sulfuric acid using copper as a reductant and iron as a catalyst. The laboratory work will be carried out on two separate laboratory days. The first day will be used for leaching and preparation of solution samples and standards for chemical analyses. On the second laboratory day, the Li and Co contents of the samples will be investigated by chemical analysis *i.e.*, atomic absorption spectrometry (AAS). The solution samples will also be titrated to determine the acid consumption during the leaching process. Before starting the lab work, the lab group will be divided into two smaller groups: Half of the group will be working on (i) the leaching experiments and titration, whereas the other half will be conducting the (ii) sample dilution, standard preparation and chemical analysis with the AAS.

*List of equipment used (Fill in the details after each item)*

* Scale – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Overhead stirrer – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Water bath – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Pt vs. Ag/AgCl reference electrode – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Multimeter – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Syringe filter – Material, Pore size, Manufacturer (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Filter paper – Manufacturer, Grade (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Oven – Brand, Model (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* AAS – Brand, Model (day 2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Magnetic stirrer (titration; day 2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

*List of chemicals used (Fill in the details after each item, sulfuric acid as an example)*

* Sulfuric acid – Purity, Manufacturer (day 1) \_\_ 95–97% H2SO4, VWR chemicals\_\_\_\_\_\_\_\_\_\_\_
* LiCoO2 – Purity, Manufacturer (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* FeSO4 – Purity, Manufacturer (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Cu powder – Purity, Manufacturer (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Nitric acid – Concentration, Manufacturer (day 1) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* NaOH solution – Concentration, Manufacturer (day 2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
* Methyl orange solution – Concentration, Manufacturer (day 2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**Students are responsible for actively recording all the measured, analyzed and weighed data to get the necessary values for the report.**

**First lab day**

*The following calculations of needed chemicals should be conducted by each student BEFORE the first lab day. See* ***Useful numbers for calculations*** *on page 4 for molar masses.*

* We will use 0.02 mol FeSO4·7H2O as catalyst. How much is that in grams?
* We will use Cu as reductant. The molar amount of Cu vs. LiCoO2 is either 1/2 (Groups A, B & C) or 1/4 (Group D, E, F & G). How much is that for your group in grams (when the mass of LiCoO2 is 10 g)?
* The stock standard solutions for AAS contain 1000 mg/l of the respective metal (Co, Li or Cu). How much of the stock solution do we need to add into a 50 ml flask (that will be filled with 2% HNO3) so that the metal concentration in the resulting solution is 1 ppm (1 mg/l)?

**Leaching group:** On the first day, the leaching experiment will be conducted. The goal is to evaluate the efficiency of Cu (in the form of powder) as a reductant for LCO. To do this, the leaching experiment will be run using only sulfuric acid for the first 30 minutes. During this time, all easily soluble Co and Li should dissolve, and a reductant will be needed for further dissolution. Therefore, copper powder and iron sulfate will be added to the reactor at 30 minutes to act as a reductant and catalyst. Leaching will be performed in a glass reactor (1 L), using 800 mL of 1 M H2SO4 (prepared beforehand) as lixiviant. The amount of LCO will be 10 g, and the amount of FeSO4·7H2O will be 0.02 mol. Leaching is performed under a temperature of 30 °C (Groups A, C, E & G) or 40 °C (Groups B, D & F) with 300 RPM agitation. Take a picture of the leaching setup and attach it to the report!

The dissolution progress is monitored by (1) solution samples – to be analyzed by titration and AAS – and (2) redox potential. Solution samples (6 mL) are taken at 5-, 15-, 30-, 35-, 45- and 60-minute timepoints using a syringe and hose, so that the first three samples will be taken during leaching without a reductant, and the latter three with iron sulfate and copper powder added into the solution. Redox potential of the solution is measured at the same time using a single-probe electrode and multimeter. The samples are then filtered through syringe filters and given to the AAS group for dilution.

After the leaching experiment is done, the volume of the pregnant leach solution (PLS) is measured, and the solution is filtered using a vacuum filtration assembly. Remember to measure the weight of the filter paper before filtration! After the filtration, the leach residue is collected and left to dry in an oven and weighed during the second lab day.

**AAS group:** The necessary standards will be prepared and all PLS samples diluted using 2% nitric acid. The standards to be used in the analysis are 1, 3, 5 ppm for all metals (Co, Li, Cu). All samples will be diluted with dilution ratios of 1:100 and 1:1500.

**Second lab day**

*Calculations of the needed chemicals should be conducted by each student BEFORE the second lab day*:

* The starting concentration of our leaching solution was 1 M H2SO4. Using this value as an assumption, calculate the amount of 0.5 M NaOH needed to titrate 2 mL of our sample. Notice that sulfuric acid contains two H+ groups!

On the second day, the leaching group will analyze the acid consumption from the samples by titration and weigh the dried leach residue. PLS samples will be titrated with 0.5 M NaOH, using methyl orange as indicator. Only samples of t = 15, 30, 45 and 60 min need to be titrated. The AAS group conducts elemental analysis on the samples. Co and Li will be analyzed from all samples, whereas Cu will only be analyzed from samples after addition of copper powder (35-, 45- and 60-min samples). Remember to write down the details of all the equipment and chemicals you use!

**Useful numbers for calculations**

c (95–97% H2SO4) = 18.01 mol/L

ρ (H2SO4) = 1.83 kg/dm3

c (65% HNO3) = 14.34 mol/L

M (LiCoO2) = 97.87 g/mol

M (Li) = 6.941 g/mol

M (Co) = 58.93 g/mol

M (FeSO4·7H2O) = 278.02 g/mol

M (Cu) = 63.55 g/mol

**Report**

One report from the whole group presenting and discussing results of the leaching experiment and analyses. The report shall include the topics listed below. **IMPORTANT: There is quite a lot of work, so share the tasks equally and start writing the report early!** For the number of points available for each section, see the last page.

1. **Introduction** (2–3 pages) that includes background information about:
* Lithium-ion batteries and their use.
* Current commercial processes (2–3 examples) for Li-ion battery recycling, and their pros and cons.
* Alternative reductants (2–3 examples) for Li-ion battery waste leaching that were not used in this exercise.
1. **Experimental**: This part explains in detail all equipment, procedures, and chemicals used in the lab work. Also attach a picture of the leaching setup!
2. **Results and discussion** that include the items listed below (you are allowed to divide Results and Discussion into separate chapters if you want). Remember to also discuss the results and answers! (What can we see from the figures? Why did we get such results? What could be the phenomena behind them? *etc.*). There is no need for a formal/mathematical error analysis, but if the results do not seem to make sense and/or you suspect that there has been one or multiple mistakes during the lab work you should list possible error sources and explain weird results that way.
* AAS analyses of both experiments as tables: Li, Co and Cu concentrations (mg/l) in the solution at each timepoint. Remember to consider the number of significant digits (the measurement may give you results with five decimals but that does not mean the actual precision is that high).
* The following figures from the leaching test: (i) Extractions of Co and Li into solution vs. time (as percentage, see hint below), (ii) redox potential vs. time, (iii) acid consumption vs. time.

**HINT:** Calculate the extractions of Co and Li throughout the leaching test by comparing the metal amount dissolved in solution at each sampling time to the initial metal amount in the solid sample. Solution volume at each timepoint can be determined when the final volume of the PLS is known, and evaporation of solution is assumed to be constant throughout the experiment. Remember to consider the volume of samples (taken away from the solution) when defining the solution volumes at each sampling time, as well as the amounts of dissolved metals removed during sampling.

* Estimation of the efficiency of Cu as reductant:
	1. Compare Co extraction before and after Cu powder addition: How much did the extraction increase when using Cu as reductant?
	2. How much of LCO (in percentage) was left undissolved in the experiment?
	3. How much Cu was left undissolved?
	4. What was the current efficiency of copper as reductant *i.e.*, how many % of the electrons provided by Cu were utilized for LCO reduction? **HINT:** Calculate the molar amount of electrons that was stoichiometrically required to dissolve the amount of Co that was leached after Cu addition (between 30 and 60 min) and compare it to the actual electron amount donated by Cu dissolved in the experiment: $Curr. eff. =\frac{Electrons to Co after 30 min (mol) }{Electrons from Cu (mol)}=X\%$

Keep in mind that 1 mol of Cu donates 2 mol of electrons upon dissolution:

Cu 🡪 Cu2+ + 2e-, whereas 1 mol of Co only needs 1 mol of electrons to dissolve: Co3+ + e- 🡪 Co2+.

Some of the copper will likely be consumed by side reactions, so the current efficiency should be less than 100%.

* What was the consumption of chemicals (assuming we would want to expand the system to an industrial scale)?
	1. Sulfuric acid vs. dissolved LCO (kg of pure H2SO4/kg LCO)?
	2. kg copper/kg of dissolved LCO?
1. **Conclusions** answering the following questions:
* Based on the results, is the tested method effective for leaching Li and Co from battery waste?
* Was the amount of Cu suitable or was there too much or too little?
* How do your results compare to published literature?
1. **Summary** that consists of a short recap of literature, main results and main conclusions. **HINT:** This is not the same as Conclusions. Think of this section as kind of the Abstract in a scientific article that delivers the most important findings of the work in a concise way and is understandable even when separated from the main text.
2. **References** to literature (around 5–10). In the text, you can use either the number format ‘[1]’ or author + year format ‘(Author et al., 2022)’. Emphasis is on the correct use of references, not the amount of them. The main objective of the reference list is to make the cited literature easy to find for the reader. Remember to also keep the format of the references uniform throughout the list.

**Evaluation principles**

The maximum number of points for the report is 50, divided into the following parts:

Introduction, max. 5 points

Experimental, max. 10 points

Results and discussion (together or in separate chapters), max. 15 points

Conclusions, max. 10 points

Summary, max. 5 points

Literature references, max. 5 points